A detailed study of effect of process parameters on Reduction of Metachloronitrobenzene (MCNB) using Hydrogen sulphide and Phase Transfer Catalyst

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Submitted by
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CERTIFICATE

This is to certify that the thesis entitled "**A detailed study of effect of process parameters on Reduction of Metachloronitrobenzene (MCNB) using Hydrogen sulphide and Phase Transfer Catalyst'** submitted by **Mr. Debabrata Champati**, Roll no. **110CH0065** in partial fulfilment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. Mr. Debabrata has worked on this topic from July, 2013 until April, 2014 and the thesis, in my opinion, is worthy of consideration for the award of the degree of "Bachelor of Technology" in accordance with the regulations of this Institute. To the best of my knowledge, the matter embodied in the report has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

Hydrogen sulphide (H_2S) is a corrosive and toxic gas, which poses serious health and operational risks when present in produced fluids such as condensate, gas and water. Therefore efforts have been made to remove H_2S from the sour gas. In today's world, there are a number of processes in use for treating "sour" gases containing the acid components H_2S and CO_2. The goal of the present work is to study the reduction of Metachloronitrobenzene using Hydrogen sulphide and phase transfer catalyst and to study the effect of temperature, catalyst loading, concentration of reactants and temperature on the conversion and selectivity of the product.

H_2S is generally separated from the sour gas to produce elemental sulphur. This process is known as Claus process. Although elemental sulphur is produced, the cost of this process is high because it involves stripping of the H_2S rich alkanolamine solution to give back the lean alkanolamine solution. However, if we use the absorbed H_2S solution to produce other chemicals which are beneficial to the chemical industry, then we need not spend a lot on production of elemental sulphur. Chloroanilines are of great importance when it comes to the manufacturing of dyestuffs, drugs and various types of pesticides. Chlorhexidine, which is a very important antimicrobial and bacteriocide is produced from chloroanilines. It is important component of the chemicals required for producing various types of pesticides likemonolinuron,anilofos and chlorphthali.Chloroanilines are also used in the manufacture of benzodiazepine drugs.This procedure of utilising H_2S is less costly than the production of elemental sulphur.

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ABBREVIATIONS

MCNB- Metachloronitrobenzene

MCA- Metachloroaniline

DEA -Diethanolamine

DIPA –Diisopropanoloamine

GLC -Gas Liquid Chromatography

MDEA-Methyldiethanolamine

MEA -Monoethanolamine

OVAT- One variable at a time

Ppm- Parts per million

Ppmv- Parts per million by volume

PTC -Phase Transfer Catalysis

TEA -Triethanolamine

TPC -Tri Phase Catalyst

CHAPTER 1

INTRODUCTION

1.1 SOURCES OF HYDROGEN SULPHIDE

Hydrogen sulphide is found in nature abundantly in natural gas and in traces in crude petroleum. H_2S is added to the environment by sulphate reducing bacteria. It is also produced by the action of water and acids on metal sulphides, which is given by the reaction-

$$MS + H_2O \rightarrow MO + H_2S$$

A major part of the global H_2S emissions are due to human activity. Petroleum refineries account for maximum amount of H_2S released into the atmosphere. Petroleum crude is brought about from various parts of the world which have a variety of sulphur and nitrogen content. The crude has to be made from sulphur which is done by the hydro-treating process in petroleum industries. In addition to that many units in coal processing industries produce a considerable quantity of H_2S and NH_3. The hydro-desulphurization step separates sulphur in the form of H_2S. Claus process is used to separate H_2S from the mixture of H_2S and CO_2 by absorption in a suitable solvent followed by production of elemental sulphur from H_2S. H_2S is also produced from other industries such as paper mills, tanneries and coke oven units.

H_2S is also present in traces in landfill gas emissions. The sulphate reducing bacteria comes into picture during landfill gas emissions. The amount of H_2S produced depends on a number of factors: moisture content, pH, amount of oxygen present and the sulphate source. During hydro-treatment of sour crude, hydrogen sulphide is produced in large amounts. In addition to that, during the sequence of several processes in the coal processing industries, one or more gaseous by-products containing H_2S is quite normally produced. Sometimes H_2S is present upto 90 % in natural gas which is more than acceptable. The composition of raw natural gas varies widely with the type of field from which natural gas is obtained. The H_2S content varies from 0.1 ppm to 150,000 ppm.

1.2 REASONS FOR TREATMENT OF SOUR GAS

Reasons for removal of hydrogen sulphide are:

- Hydrogen Sulphide is a poisonous and highly flammable gas. It is denser than air, therefore, it settles down at the bottom in the vicinity of the leakage site. It has a pungent smell and at the same time damages the nasal tract. A victim might be unaware of its presence which turns out to be fatal.
- H_2S is corrosive in the presence of water and poses great environmental threat in form of acid rain. Therefore, it must almost completely be removed from the gas streams before use and preferably before transport.

• Owing to its corrosive nature, presence of H_2S in the gas pipelines of refineries can cause a number of problems like corrosion of interiors of equipments, deactivation of the catalysts, unwanted side reactions and production of side products, increase in the process pressure requirements, etc.
• The process of production of sulphur is energy intensive process because of the involvement of stripping units. In addition to that, the demand of elemental sulphur is not at par with the demand, therefore the price of sulphur is very low in the market. Hence H_2S should be absorbed in alkanolamines and treated with fine chemicals to produce variety of chemicals of commercial importance.

For safe management procedures, a hydrogen sulphide material safety data sheet (MSDS) should be consulted. Different standards of H_2S emissions and its warning signs are shown in Table 1.1 and Table 1.2 respectively.

Table 1.1. Standards of H_2S emissions

Occupational Exposure Limit (8 h time weighted average)	10 ppm
Public Exposure Limit (for the general population)	0.03-0.006 ppm

Maximum Emissions Limit from Sulphur Recovery Units
• 1500 ppmv of sulphur compounds calculated as SO_2
• 10 ppmv of H_2S.
• 200 pounds per hour of sulphur compounds calculated as SO_2

Table 1.2: H_2S Warning Signs

Concentration in parts per million(ppm)

Observations and health effects

Less than 1	Most people smell "rotten eggs."
3-5	Odour is strong.
20-150	Nose and throat feel dry and irritated. Eyes sting, itch, or water; and "gas eye" symptoms
150-200	Damages nasal tract
200-250	Nausea, vomiting and headache occurs. Pulmonary edema develops, which can be fatal.
300-500	Symptoms are the same as above, but more severe which might result in death.
Above 500	Immediate loss of consciousness. Death is likely to be immediate.

1.3 INDUSTRIAL PROCESSES FOR THE REMOVAL OF H_2S

1.3.1 Hydrogen sulphide absorption using Alkanolamine

The absorption of Hydrogen sulphide using alkanolamines is the most significant process which helps in recovering elemental sulphur from gaseous hydrogen sulphide. It is also known as the Claus process. This process was patented in 1883 by the scientist Carl Friedrich Claus. Now it is widely in use to produce elemental sulphur. H_2S gas separated from the host gas stream using amine extraction is fed to the Claus unit, where it is converted in two steps:

1. <u>Thermal Step</u>: This step is all about the reaction between the H_2S rich gas and air.It is generally carried out in a furnace at high temperature (1000 – $1400^{O}C$). The reaction 1.1 takes place in the furnace at such high temperature. The acid gases with no more combustible contents apart from hydrogen sulphide are burnt in burner by the following chemical reaction:

$$2\ H_2S + 2\ O_2 \rightarrow SO_2 + 2\ H_2O + S \qquad \text{.... (1.1)}$$

This is a highly exothermic reaction which generates sulphur dioxide. The ratio of air to the acid gas is maintained in such a manner that only one third of all hydrogen sulphide is converted to SO_2.

2. **<u>Catalytic Step</u>:** The product gas is then heated to a temperature of $350^{O}C$ and is sent to a series of catalytic converters where hydrogen sulphide reacts with sulphur dioxide to produce elemental sulphur and water vapour is released.

$$2\ H_2S + SO_2 \rightarrow 3\ S + 2\ H_2O \qquad \text{.... (1.2)}$$

Activated aluminium (III) or titanium (IV) oxide is generally used as the catalyst.Sulphur produced is used for production of pesticides and sulphuric acid. It also is an imporatant component in the production of medicine, cosmetics, fertilizers and rubber products.

However, the Claus process has a number of inherent disadvantages. Forexample:

- High operating temperatures are required which consume a lot of energy.
- The ratio of oxygen to H_2S in the feed has to be controlled accurately.
- The energy contained in hydrogen is lost..
- A portion of the CO_2 must be removed from the byproduct gas by pre-treatment before oxidizing the H_2S.

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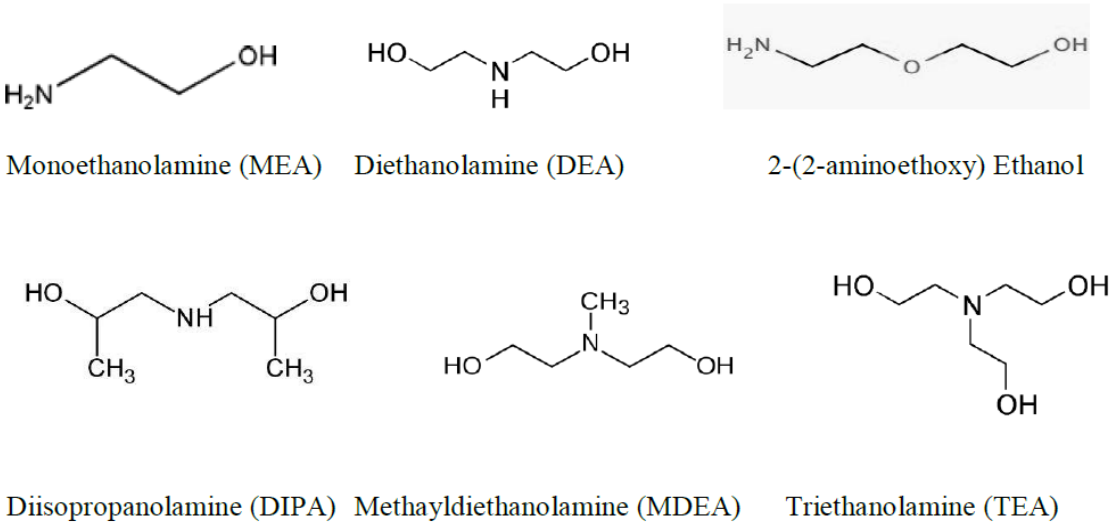


Monoethanolamine (MEA) Diethanolamine (DEA) 2-(2-aminoethoxy) Ethanol

Diisopropanolamine (DIPA) Methayldiethanolamine (MDEA) Triethanolamine (TEA)

Fig 1.1 Structural Formulae of variousAlkanolamines used for absorption of H_2S

Advantages of MDEA in gas treating:

- Alkanolamines can be used in higher concentrations, hence, they have a greater capacity to react with acid gases.
- They are selective in nature and react with most of the H_2S while reacting with a very little amount of CO_2.They increase the capacity of existing units and allow equipments to be considerably smaller for new units.
- Alkanolamines reduce the energy consumption in a process unit.

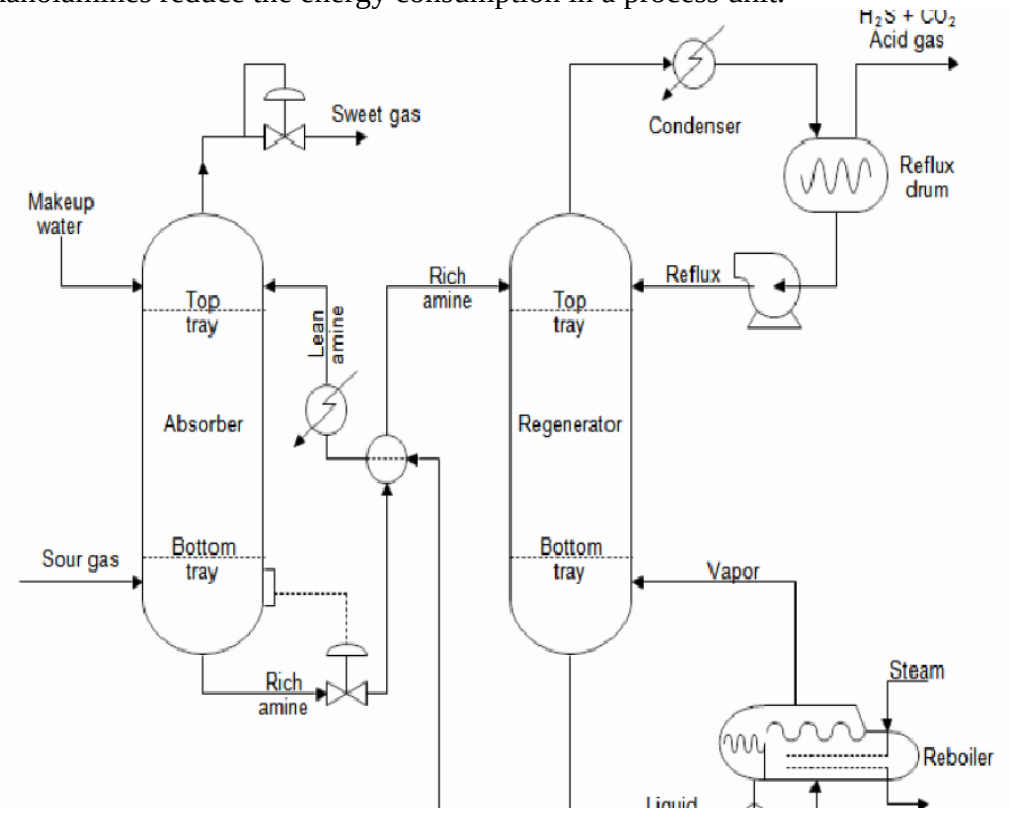


Fig 1.2 Flow diagram for separation of H_2S from sour gas

1.3.2 Ammonia based process

Usage of aqueous ammonia in the elimination of H_2S from gas streams had been wellpracticed by Hamblin, Harvey and Makrides. Gas streams comprising both H_2S and NH_3 pass through scrubber which removes H_2S followed by a scrubber which removes NH_3 in sequence.Water is sprayed from the top of the NH_3scrubber to absorb ammonia from the gas. The solution thus obtained from the first scrubber is used as an absorbent for H_2S in the H_2S scrubber. Ammonium sulphide is formed as a result of the reaction of hydrogen sulphide and ammonia which is then sent to a deacidifier, which separates the ammonium sulphide to yield the vapour which is rich in H_2S and a liquor rich in NH_3.The usage of ammonia to remove H_2S and $CO_2$from sour gas has declined in this decade; however, the process is still used for byproduct recovery in most of the coke oven units. The reactions happening inthe system comprised of ammonia, hydrogen sulphide, and water can be represented by thefollowing equations:

$$NH_3 + H_2O = NH_4OH \quad \text{....(1.3)}$$

$$NH_3 + H_2S = NH_4HS \quad \text{....(1.4)}$$

$$2NH_3 + H_2S = (NH_4)_2S \quad \text{....(1.5)}$$

The NH_3-based process is appropriate for gas streams comprising both H_2S and NH_3,as simultaneous removal of NH_3 is obvious in this process. Besides, for the gas streams containing both H_2S and NH_3, the removal of both impurities might becompleted in a solitary step in the ammonia-based process instead of two steps as in the situation of alkanolamine-based process.

Advantages of the Ammonia based process:

The rate of absorption of H_2S into aqueous NH_3 solution is fast and reliant upon theconcentration of NH_3. Therefore, with acceptable NH_3 concentration at the interface,it is possible that the resistance of the gas film governs the H_2S absorption rate. The absorption of CO_2 in weak alkaline solution like aqueous NH_3 isa liquid film controlled system. Therefore $H_2S$is absorbed at higher rate than CO_2. Hence, the use of aqueousNH_3, ensures the selective absorption of H_2S or CO_2. By the practice of spray column in combination with short contacttime can lead to the selective absorption of H_2S from the gas mixture containing bothCO_2 and H_2S.

Problems associated with operation of Ammonia based process:

Dilute NH_3 solution is required to wash because of the high partial pressure of ammoniaor a separate water wash step after the NH_3 scrubbing step in order to remove ammonia from the treated gas stream. The cost of regeneration increases as it is carried out at high temperature.

Sulphur product gets contaminated with the catalyst as the scrubbing step involves the use of soluble catalysts if the regeneration of rich absorbent solution is withdrawn.

1.3.3 CrystaSulf Process

Removal of hydrogen sulphide from natural gas and gas streams of refineries and chemical plants is done by a complex chemical process called CrystaSulf process. This process is similar to that of Claus process with the respect to the mechanism, but this process makes use of the Claus reaction in the liquid phase to produce sulphur which can be separated by filtration. It is generally used as an one-step alternative to Amine–Claus process.

1.3.4 Wet-oxidation LO-CAT Process

Iron catalyst is used to convert hydrogen sulphide to elemental sulfur in wet oxidation LO-CAT process. Precipitation of iron sulphide/ iron hydroxide is prevented while the catalyst is held in solution by organic chelating agents. LO-CAT solution is used to oxidise hydrogen sulphide to sulphur by reduction of iron. The reduced iron ions are then transferred from the absorber to the oxidizer where the ferrous iron undergoes oxidation to ferric iron by oxygen from atmosphere, absorbed into the solution, thus regenerating the catalyst.

1.4 PHASE TRANSFER CATALYSIS

Whenever there are more than two phases, then the reaction becomes less feasible. This is because the interaction between both the phase decreases. For a reaction to occur the two phases should interact with each other. For immiscible phases this does not happen, hence a phase transfer catalyst is used. A phase transfer catalyst provides active sites for the reaction to take place. Hence, phase transfer catalysis denotes the increase in the rate of reaction of an otherwise slow reaction due to little interaction between the two phases. By using a phase transfer catalyst, the rate of reaction can be increased, the conversion of the reactant to product can also be increased and it eradicates the need of expensive solvents which convert all the immiscible phases into one phase by dissolving all the reactants. By using phase transfer catalysis we can minimize the production of by products or side products, consequently minimizing the amount of wastes produced from the reactions. It reduces the use of organic solvents for converting all the reactants into one phase.

PTC can be used for liquid-liquid and liquid-gas operations. Quaternary onium salts are used as catalysts fortransferring anions in PTC reactions. Quaternary ammonium salts are easily available and are cheaper as compared to other phase transfer catalysts, hence, widely used.. The ease of extraction of the ion, the stability of the ion and the trpsort characteristics of the ion in both organic and aqueous phases and at the interface are the factors to be considered before choosing a particular catalyst. .Present study was carried out using Amberlite IR 400 as PTC.

1.4.1 Interfacial Mechanism of Phase-Transfer Catalysis

Phase transfer catalysts (PTC) help in carrying the highly active species (for penetrating theinterface), into the other phase where the reaction takes place, which results in high conversion andselectivity for the desired product even under mild reaction conditions. This type of reaction wastermed “phase-transfer catalysis” (PTC) by Starks in 1971. PTC is used in a variety of reactions which involves two immiscible phases, e.g., addition reactions, reduction reactions, hydrolysis, alkylation, oxidation reactions, etherification, esterification, carbene, and chiral reactions(Starks 1997).

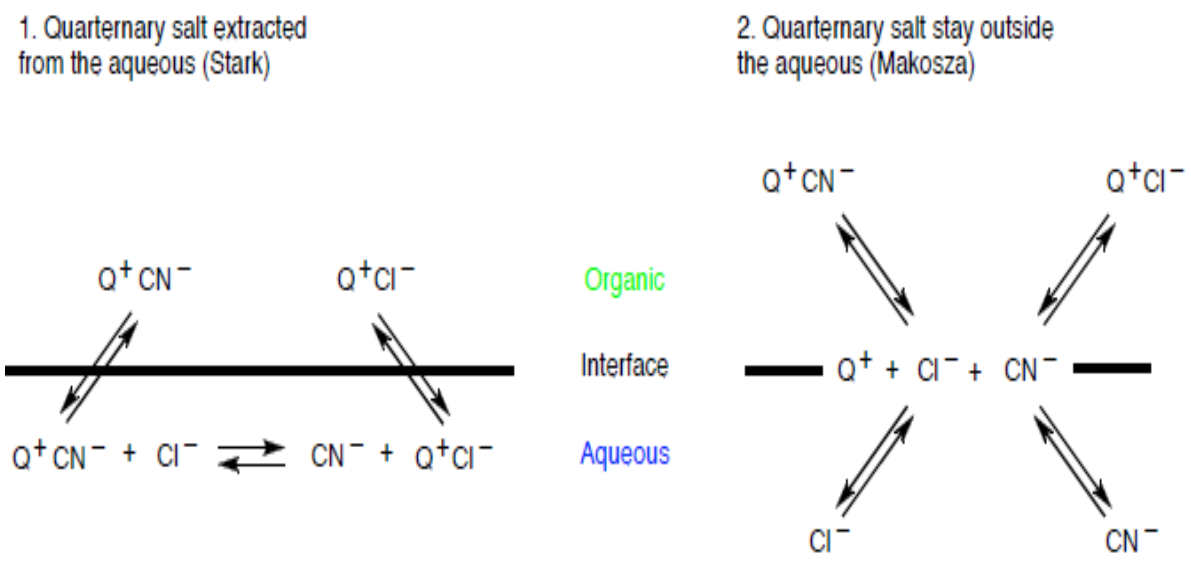


Fig 1.3 Mechanisms of Phase Transfer Catalysis

(Source: Presentation,MacMillan Lab. Group Meeting, Phase Transfer Catalysis)

Liquid Liquid Solid Phase Transfer Catalyst:

It is a solid catalyst. The supported catalyst can be easily separated from the final product and the unreacted reactants simply by filtration orcentrifugation, therefore it can be used in industries for carrying out phase transfer reactions. Both plug flow reactor or a continuous stir tank reactor can be used in this case.

1.4.2 Mechanism of LLSPTC

The mechanism for a liquid-liquid-solid phase transfer catalysis reaction is as follows:

(A) Masstransfer of reactants from the bulk solution to the surface of the catalyst pellet,

(B) Diffusionof reactant to the interior of the catalyst pellet (active site) through pores, and

(C) Intrinsic reaction of reactant with active sites.

Triphase catalysis is a complex form of catalysis, because it involves not merely diffusion of a single gaseousor liquid phase into the solid catalyst. The organic phase, as well as the aqueous phase co-exist, inside the pores of the catalyst polymer. A number of reactions take place in the organic phase, aqueous phase and at the interface of the organic and aqueous phase.. The working of a catalyst is lipophilic in nature. The interaction between the salts and the different phases play a vital role in influencing the reaction rate.

1.5 OBJECTIVE OF THE PROJECT:

The present work is done with the view of producing an alternative to Claus or LO-CAT process for better utilization of H_2S present in various gas streams.The goal of the present work is to study the reduction of metachloronitrobenzene using hydrogen sulphide and phase transfer catalyst and to study the effect of temperature, catalyst loading, concentration of reactants and temperature on the conversion and selectivity of the product.

The present investigations are devoted to:

- Synthesis of value-added fine chemicals like chloroanilines using the H_2S-rich aqueous ammonia and/or alkanolamines under tri phase (liquid-liquid-solid) conditions in the presence of a phase transfer catalyst (PTC), Amberlite.
- Study how the process variables (stirring speed, catalyst loading, concentration of reactant, and temperature, alkanolamine concentration, elemental sulphur loading) affect the conversions of organic reactants and selectivity of various products.
- Find out a suitable mechanism utilizing the variation of reaction rate and conversion with the various controlling parameters, to justify the path of the reaction.
- Kinetic modelling of the above mentioned commercially important reactions and estimation of the model parameters.

1.6 CHAPTER LAYOUT:

The thesis is divided into 6 chapters. The present chapter is regarding the introduction to the project work and the reasons behind choosing the topic. It describes the usefulness of the topic by presenting the uses of the product of the reaction. It also depicts the advantages of the process described over other similar processes.

Chapter 2 throws light on the literature review about reduction of nitro compounds, use of aqueous alkanolamines to absorb H_2S and the kinetic modelling of the reaction already carried out by scientists and professors from reputed institutes.

Chapter 3 describes the experiment to be carried out, its procedure, experimental setup required and how the initial calculations are to be done

Chapter 4 is regarding the observations made throughout the course of the experiment and the results obtained from the same. It also includes comparison of the result data to make it more informative.

Chapter 5 concludes the work done in the project in a systematic way to focus upon the results obtained and their usefulness.

Chapter 6 throws light on the future scope of the project and how this project will help in the development of an industrial model for the use of hydrogen sulphide to produce fine chemicals with wide commercial applications.

CHAPTER 2

LITERATURE REVIEW

2.1 USE OF AQUEOUS ALKANOLAMINES FOR THE REMOVAL OF H_2S

Kohl and Nielsen had studied the separation of H_2S and its retrieval from process gas streams by ammonium hydroxide in 1997. Thisprocess was established by Hamblin, 1973 for removal of hydrogen sulfide from gas streams usingammonium hydroxide to produce ammonium hydrosulphide. The ammonium hydrosuphide thus produced was oxidised by an air stream to get an effluent stream containing ammoniumpolysulphide and treating the ammoniumpolysulphide containing stream to recover elemental sulphur. In recent times, Asai et al. (1989) studied the rates of simultaneous absorption of H_2S and ammonia into water in an agitated vesselwith a flat interface and Rumpf et al. (1999) studied the simultaneous solubility of ammonia andH_2S in water at temperatures from 313 to 393 K and total pressures up to 0.7 MPa. Recently, aqueous alkanolamines have been in use in industry for the removal of hydrogen sulfide from sourgas streams.

2.2 REDUCTION OF NITROAROMATICS

Prof. Sunil K. Maity, Narayan C. Pradhan and Anand V. Patwardhan studied the kinetics of reduction of Nitrochlorobenzenes under liquid –liquid phase transfer catalyst. Toluene was used as a solvent and the catalyst used was TBAB (tetrabutyl ammonium bromide). Overall conversion of PNCB decreases with increase in concentration of PNCB. Order of the reaction was obtained to be 1.2. Reaction rate increased with increase in sulphide concentration. Overall conversion of PCNB (after prolonged reaction run) was found to increase with increase in ammonia concentration.

Prof. Sunil K. Maity, Narayan C. Pradhan and Anand V. Patwardhan carried out the reduction reactions of nitrochlorobenzenes (NCBs) with aqueous ammonium sulphide in toluene, under liquid-liquid mode with phase transfer catalyst, tetrabutylammonium bromide (TBAB). The product compound was chloroanilines and its selectivity was 100%. The reaction rate of m-nitrochlorobenzene (MNCB) was found to be highest among the three NCBs followed by o- and p- nitrochlorobenzene (ONCB and PNCB). The reaction was found to be kinetically controlled with activation energies of reactants in the specific reactions found to be 22.8, 19.6 and 9.4 kcal/mol for ONCB, PNCB and MNCB, respectively. The effects of different parameters such as concentration of NCB, TBAB concentration, sulphide concentration, ammonia concentration, and elemental sulphur loading on the reaction rate and conversion were studied to establish the mechanism of the reaction. The rate of reaction of NCBs was found to be proportional to the concentration of catalyst and NCBs and to the cube of the concentration of sulphide.

Bamfield and Sutcliffe(1978) have prepared a number of organic sulphides/disulphidesby the reaction of different activated aryl halideswith aqueous sodium sulphide/disulphide in the presence of benzyl triethyl ammonium chloride as the phase-transfer catalyst. Bhave and Sharma (1981) have studied the kinetics of two-phase reduction of m-chloronitrobenzene by aqueous solutions of sodium sulphide/disulphide without using anycatalyst.

The reduction of o-nitro- and p-nitrochlorobenzene with sodium sulphide was carried out by Shner et al. (1989). The reaction was carried out in the absence as well as in the presence of phase-transfer catalyst TBAB (tetrabutyl ammonium bromide). Tetrabutylammonium bromide (TBAB) and polyethy1ene glycol-400 (PEG-400) were the two phase transfer catalysts used in this case. According to Timokhin and Kissin,1966; and Bhave and Sharma, 1981, the reaction of metachloronitrobenzene (MCNB) with sodium sulphide gives m-chloroaniline (MCA) as the only product.

In the *case* of o-nitro- and p-nitrochlorobenzene (ONCBand PNCB), because of the electron withdrawing effect of the nitro group, the chlorine atom is activated and their reaction with sulphide can give rise to substituted products, namely, dinitro diphenyl sulphides. It may be possible to change the course of the reaction from one product to another by using a phase-transfer catalyst and suitably manipulating the experimental conditions. The only information in the literature on the use of phase-transfer catalysts to change the selectivity of a reaction is the asymmetric syntheses via chiral phase-transfer catalyst (Dolling et al., 1987; Soaiand Watanabe, 1990).

Sunil K. Maity, Narayan C. Pradhan and Anand V. Patwardhan used H_2S-rich aqueous diethanolamine (DEA) solution to convert o-nitro anisole to o-anisidine along with the production of sulphur. The reduction of o-nitroanisole was done with the help of TBAB as the liquid-liquid phase transfer catalyst. This reaction was carried out to analyse the variation of the rate and cobnversion of the reaction with change in DEA concentration and the elemental sulphur loading. After this analysis, the stoichiometry and mechanism of the Zinin reduction reaction using H_2S-rich aqueous DEA was established. The reaction was found to be kinetically controlled with activation energy of 63.6 kJ/mol. The rate of reaction of ONA was also found to be proportional to the concentration of catalyst, to the cube of the concentration of ONA, and to the 1.63 power of the concentration of sulphide. An empirical kinetic model based on experimental observations was developed to correlate the experimentally obtained conversion versus time data.

There are a lot of methods in practice for the reduction of nitroarenes. One of the oldest and traditional methods is the Bechamp reduction. This reduction eaction uses finely divided iron metal and water in presence of small amounts of acids. The iron sludge thus produced in the reaction is difficult to filter and its disposal may lead to a lot of environmental hazards. It cannot be used for the reduction of a single nitro group in a polynitro compound.

Another method used for the reduction of nitroarenes is the process of catalytic hydrogenation. This method requires greater capital investment in form of expensive equipments. Furthermore, the catalyst processing is costly and the catalyst is prone to be

poisoned. Metal hydrides like lithium, aluminium hydride generally convert nitro compounds to a mixture of azoxy and azo compounds but this process is quite expensive too.

When nitroarenes are reduced by negative divalent sulphide ions, then the reduction reaction is known as Zinin reduction (Dauben, 1973). The kinetic modelling of this type of reduction reactions of nitroarenes using sodium sulphide and sodium disulphide both in the absence and in the presence of phase transfer catalyst (PTC) under different modes of phases (solid‑liquid and liquid‑liquid) have been studied by scientists and researchers. Hojo et al., 1960, Bhave and Sharma, 1981, Pradhan and Sharma, 1992 and Pradhan, 2000; Yadav et al., 2003a and Yadav et al., 2003b have studied the Zinin reduction reaction.

S.K.Maity et al. used anion exchange resin as a liquid-liquid-solid tri phase transfer catalyst to carry out the reduction of para nitrotoluene by aqueous ammonium sulphide. The liquid – liquid-solid tri phase transfer catalyst used in this case was Seralite SRA 400 (Cl-form). They inferred that the reaction was kinetically controlled with apparent activation energy of 49.8 KJ/mol. They found out the relationship between rate of reduction of para nitrotoluene and concentration of the reactant and sulphide. The rate of reduction was proportional to the square of the concentration of sulphide and to the cube of the concentration of para nitrotoluene. They developed an empirical kinetic model to correlate the experimentally obtained conversion versus time data.

Knowledge gap

No attempt has been made in the past to prepare chloroanilines from reaction of nitrochlorobenzene with H_2S -rich aqueous alkanolamine by using phase transfer catalyst. Moreover, there is no published work on the detailed kinetic study of preparation of chloroaniline from nitrochlorobenzene using H_2S -rich aqueous alkanolamine under tri-phase conditions in the presence of a PTC.

CHAPTER 3

EXPERIMENTAL

3.1 CHEMICALS AND CATALYST

Kipp's apparatus is used in the laboratory for the production of Hydrogen sulphide which is absorbed in MEA solution. Sulphidecontent of the solution is estimated by iodometric titration method. Other reagents, including analytical grade toluene (≥ 99.5 %)was acquired from Merck (India) Ltd., Mumbai. Amberlite, the catalysts for the reduction reactionwere procured from Merck (India) Ltd., Mumbai. Monoethanolamine (≥98 %) and chloronitrobenzenes were obtained from Merck (India) Ltd., Mumbai,India. Iron (II) sulphide (FeS) sticks were obtained from Sigma Aldrich, Mumbai, India. Also,the chemicals used for iodometric titration for the estimation of sulphide content i.e., sodium thiosulphate, potassium iodate, potassium iodide, starch powder, sulphuric acid (98 % pure) andsodium hydroxide pellets of analytical grade were obtained from Merck (India) Ltd., Mumbai.

3.2 PREPARATION OF H_2S RICH AQUEOUS ALKANOLAMINES

Initially, for obtaining a H_2S-rich aqueous monoethanolamine (MEA) of around 30-35 wt% aqueous alkanolamine solution was obtained by adding a suitable quantity ofdesired alkanolamine in distilled water. Then H_2S gas produced in the Kipp's apparatus as shown in the figure, was released into this aqueous alkanolamines in a 250 mL standard gasbubbler. H_2S gas was prepared in laboratory scale in Kipp's apparatus by reacting FeS sticks with H_2SO_4. The concentration of H_2SO_4 was taken as 1 molar and the reaction carried out inKipp's apparatus is as follows:

$$FeS + H_2SO_4 \xrightarrow{exothermic\ reaction} H_2S\,(g) + FeSO_4 \qquad \text{....(1)}$$

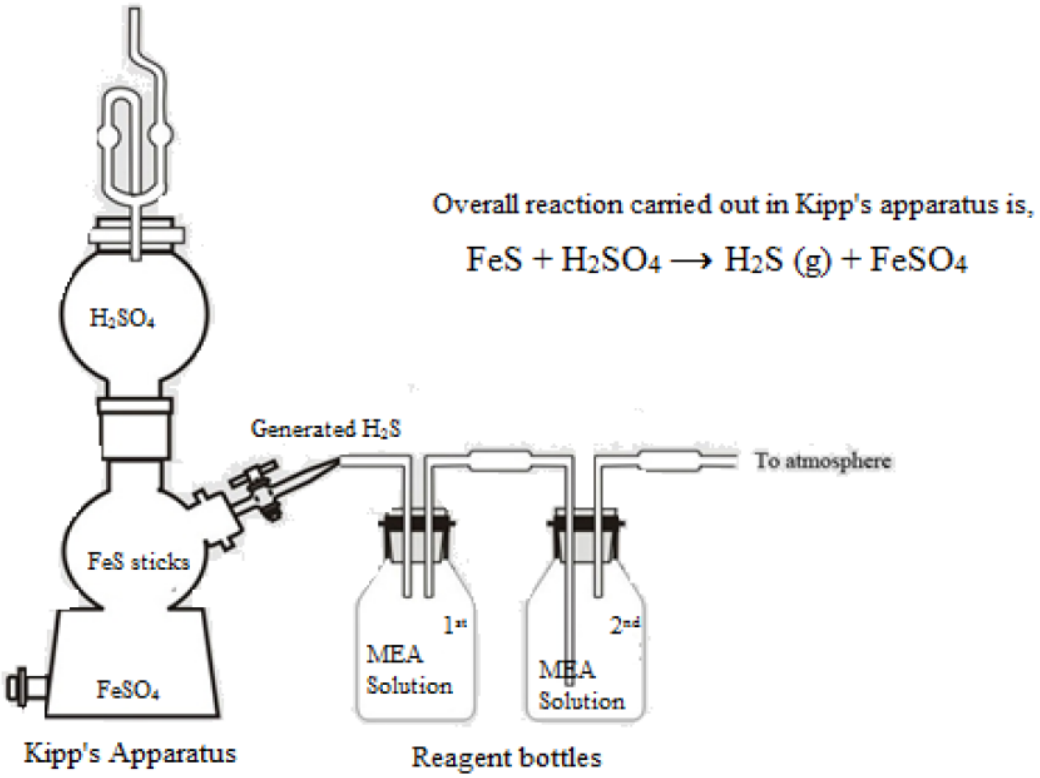


Fig 3.1 Schematic diagram for the absorption of H_2S in MEA solution

The reaction of H_2S with alkanolamines is exothermic (Kohl and Nielsen, 1997), hence, the gas bubbler containing aqueous alkanolamine was kept immersed in an ice water bath in order to prevent the oxidation of sulphide which results in the formation of disulphide. The unabsorbed H_2S gas from the first bubbler was sent to another bubbler containing ~ 1M MEAsolution whose outlet was open to the atmosphere. Liquid samples were withdrawn from at regular intervals of time after the bubbling of gas stopped and the samples were analysed for sulphide content (Scott,1966). The bubbling of gas was continued until the requiredsulphide concentration was obtained in the aqueous alkanolamines.

3.3 DETERMINATION OF SULPHIDE CONCENTRATION

Initial sulphide concentrations were determined by standard iodometric titration method (Scott,1966) as given:

Preparation of standard (0.025 M) KIO_3 solution:

A standard solution was prepared by accurately weighing 4.28 gm of KIO_3 and dissolving it in distilled water. The volume was made up to 1 L in a graduated volumetric flask.

Preparation of standard (0.1 M) sodium thiosulphate solution:

A standard sodium thiosulphate solution is prepared by accurately weighing 25 gm of $Na_2S_2O_3.5H_2O$crystals and dissolving it in distilled water. The volume is made up to 1 L in a graduatedvolumetric flask with distilled water. About 0.1 g of sodium carbonate or three drops ofchloroform was added to this solution to keep the solution for more than a few days.

Standardization of sodium thiosulphate solution by standard potassium iodate solution: 25mL of 0.025M KIO_3solution was taken and 1 gm (excess) of potassium iodide (KI) was added toit followed by 3 mL of 1 M sulphuric acid. The liberated iodine (I_2) was titrated with thiosulphatesolution. When the colour of the solution became a pale yellow, it was diluted to ca. 200 mL with distilled water. 2 mL of starch solution was added, and the titration was continued until the colourchanged from blue to colourless. The chemical reaction involved in this titration is given below.

$$KIO_3 + 5KI + 3H_2SO_4 \rightleftharpoons 3I_2 + 3H_2O + 3K_2SO_4 \quad \text{....(2)}$$

$$2Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + 2NaI \quad \text{....(3)}$$

Therefore, 1 mole of $KIO_3 \equiv 3\times2$ mole of $Na_2S_2O_3$.

$$\therefore Strength\ of\ thiosulfate\ soluton = \left(\frac{6 * strength\ of\ KIO_3 * volume\ of\ KIO_3}{volume\ of\ thiosulfate\ consmed}\right) \quad \text{....(4)}$$

Estimation of sulphide concentration:

15 mL of standard (0.025M)potassium iodate solution was taken in a conical flask. 10 mL of sulphide solution containingabout 2.5 mg of sulphide was then added to it followed by the addition 10 mL of 10M sodiumhydroxide solution. The mixture was boiled gently for about 10 minutes, cooled, and 5 mL of KIsolution and 20 mL of 4M sulphuric acid solution were added to it. The liberated iodine was titrated, which was equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulphate in the usual manner. The potassium iodate in the alkaline medium oxidizes the sulphide to sulphate as given by the following reaction. For sulphide solution having sufficiently high sulphide concentration, suitable dilution was made before the estimation of sulphide by above mentionedprocedure.

$$4IO_3^- + 6OH^- + 3S^{2-} = 3SO_4^{2-} + 4I^- + 6H_2O \quad \text{....(4)}$$

$$4\ mole\ of\ IO_3^- \equiv 3\ mole\ of\ S^{2-}$$

$$H_2S\ concentration = \left\{\left[(15 * S_{iodate}) - \frac{(V_{thiosulfate} * S_{thiosulfate})}{6}\right] * \frac{3}{4} * \frac{N_d}{10}\right\} \quad \text{....(5)}$$

Where S_{iodate}= Strength of KIO_3

$V_{thiosulfate}$ = Volume of thiosulfate

$S_{thiosulfate}$= Strength of thiosulfate

N_d= Number of times of dilution

3.4 REACTOR SETUP

The design of a typical reactor is as shown in the fig. All the reactions are to be carried out in a thermostated (± 0.5 ^{0}C)three-necked 250-ml (6.5 cm I.D.)in a batch mode equipped in a fully baffled mechanicallystirred glass reactor. The reactor is mechanically agitated using a 2.0 cm-diameter six-bladed glass disk turbine impeller the speed of which can be regulated manually. The blades of the stirrer are positioned at a height of 1.5 cm from the bottom which ensures efficient stirring of the reaction mixture. Borosilicate glass beaker would be used as the contactor and three-necked flask,a dropping funnel serving the purposes of agitating the solution, inserting the thermometer,taking samples, and feeding the feed. The motto is to reduce the building up of mass transfer resistance. This arrangement ensures excellent solid-liquid mixing for high mass transfer rate. The reactor assembly is to be kept in a constant temperature water bath whosetemperature could be controlled within ± 0.5 ^{0}C and mechanically stirred at a known speed withan electric motor.

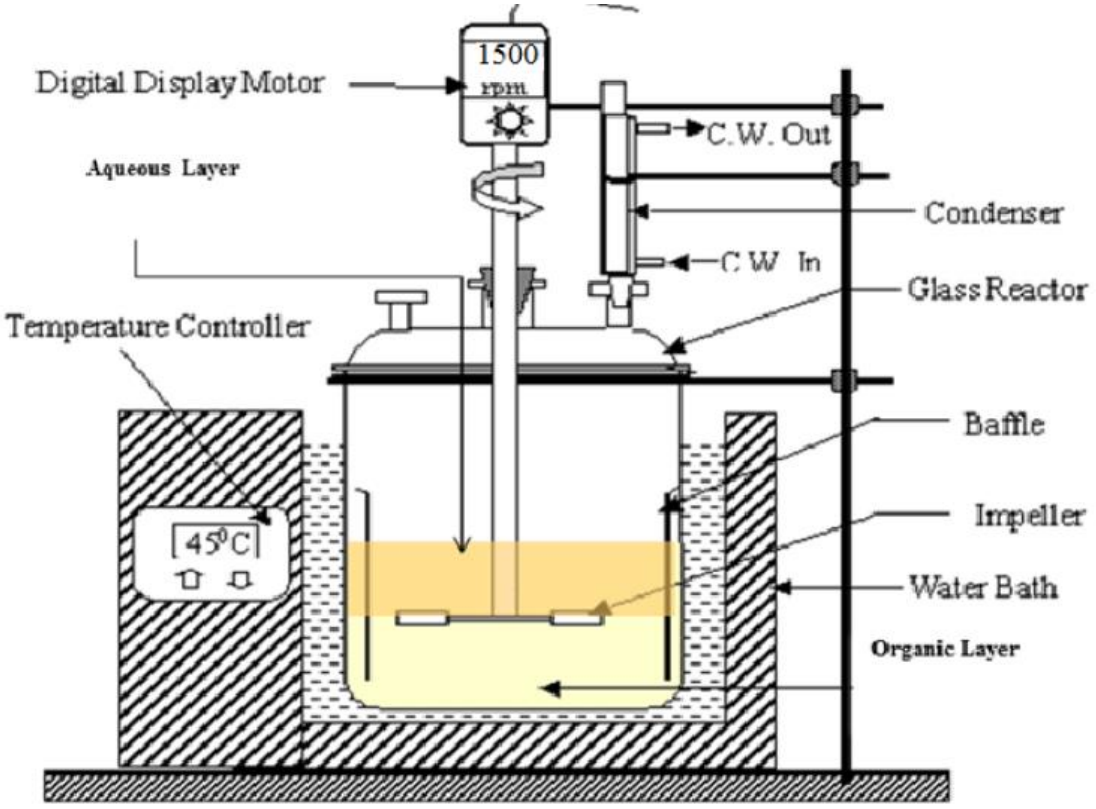


Fig 3.2 Outline of a Typical Reactor

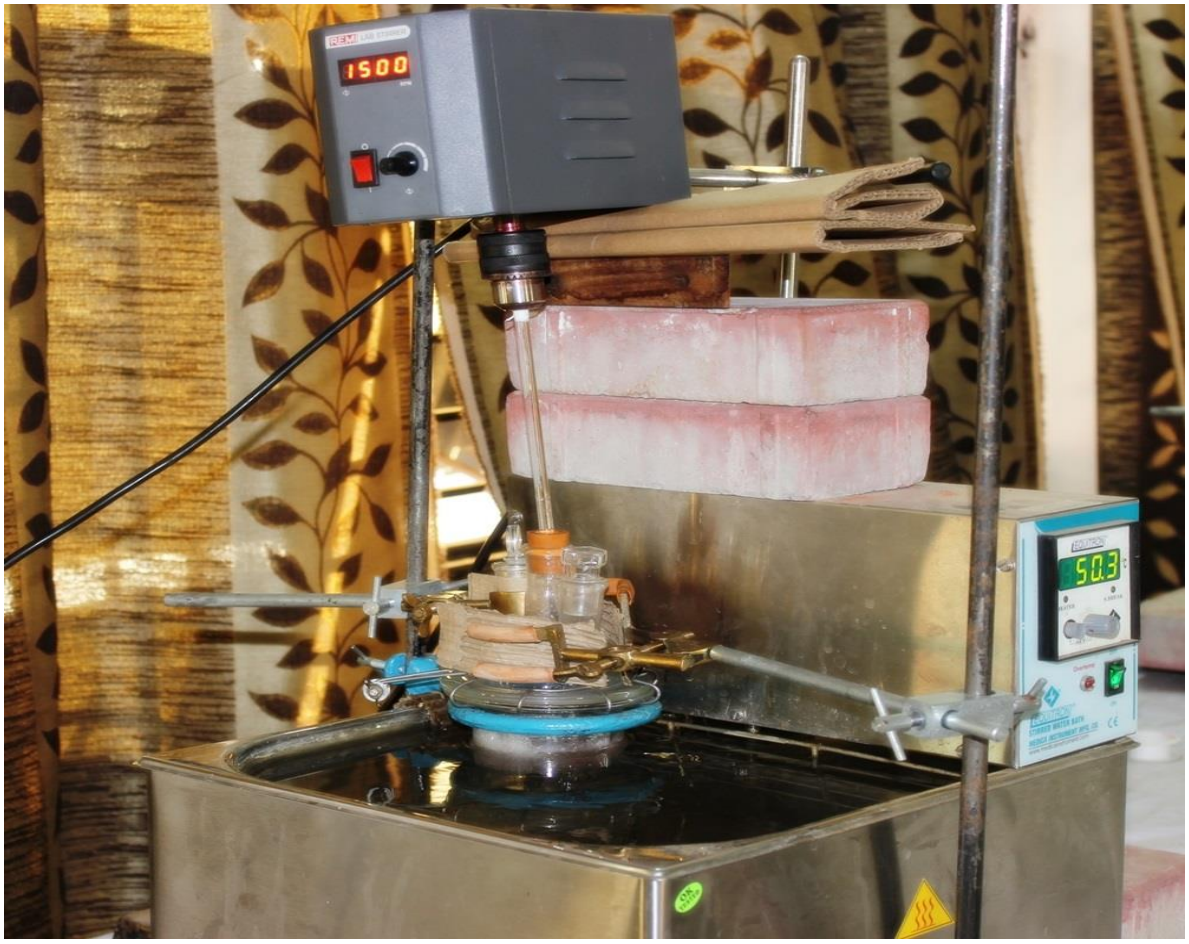


Fig 3.3 The apparatus in the laboratory for carrying out the reaction

3.5 REACTION PROCEDURE

Reaction procedure for nitrochlorobenzene reduction:

- H_2S gas was prepared in the laboratory using Kipp's Apparatus followed by absorption in MEA solution. The MEA solution of 30-35 weight% was prepared adding required amount of water to MEA.
- Iodometric titration was performed to find out the sulphide ion concentration.
- Organic phase was prepared by adding toluene to 10 grams of MCNB so that the volume becomes 50 ml.
- Aqueous phase was prepared by dissolving 3 gram of sulphur in 50 ml of H_2S-MEA solution, along with it 10 grams of Amberlite was taken in the reactor.
- The organic phase, aqueous phase and the catalyst were fed into the reactor. Aqueous phase was added first followed by organic phase.
- The reactor was immersed in an isothermal water bath.
- The temperature was maintained at 50 ^{0}Cand stirring speed is gradually increased to 1500RPM after the system was switched on.

- 9 samples of volume 0.1 ml each were collected at 5 min, 10 min, 15 min, 30 min, 60 min, 120 min, 240 min, 360 min and 480 min time duration. Before the collection of the sample, stirring was discontinued and 5 min time was allowed for the contents to settle down into two phases.
- The product so obtained was analysed in the gas chromatograph.
- One variable at the time approach was followed for each experiment. Catalyst concentration, reactant concentration, temperature and stirring speed are varied one at a time for each experiment and all the above steps were repeated for each of the experiment.

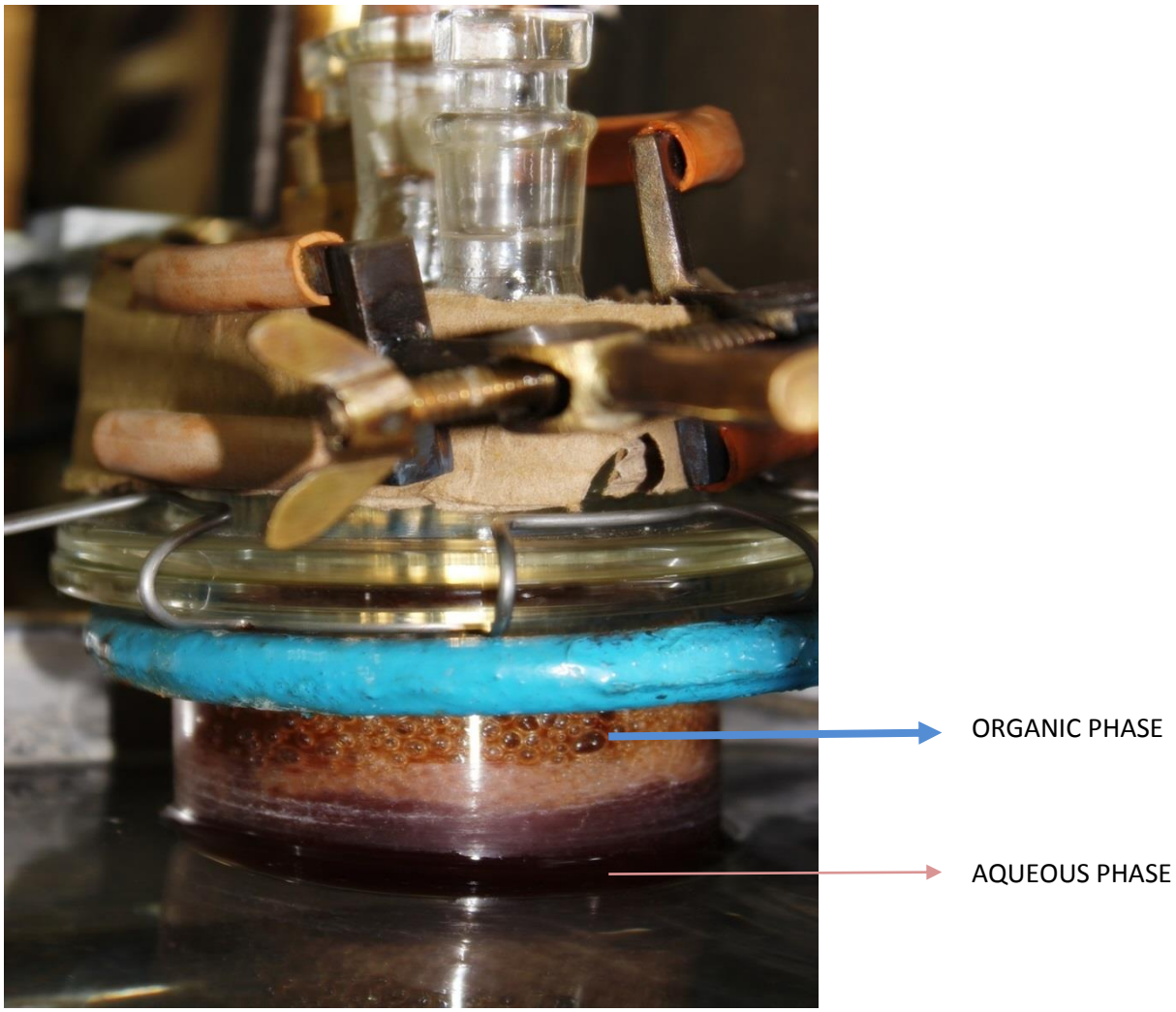


Fig 3.4 Separation of phases in the reactor

3.6 GAS CHROMATOGRAPHY (GC)

Gas chromatography is a complex chromatographic technique to separate volatile organic compounds. A gas chromatograph consists of a flowing mobile phase, an injection port, a separation column containing the stationary phase, a detector, and a data recording system. The organic compounds are separated due to differences in their partitioning behaviour between the mobile gas phase and the stationary phase in the column.

The graph of Response to Retention time is obtained from the Gas Chromatograph. The chromatograph has to be calibrated with a pure sample whose molar concentration is already determined beforehand.

The graph of Response to Retention time of a pure sample of solution of toluene and metachloronitrobenzene is as shown in the figure Fig 3.5:

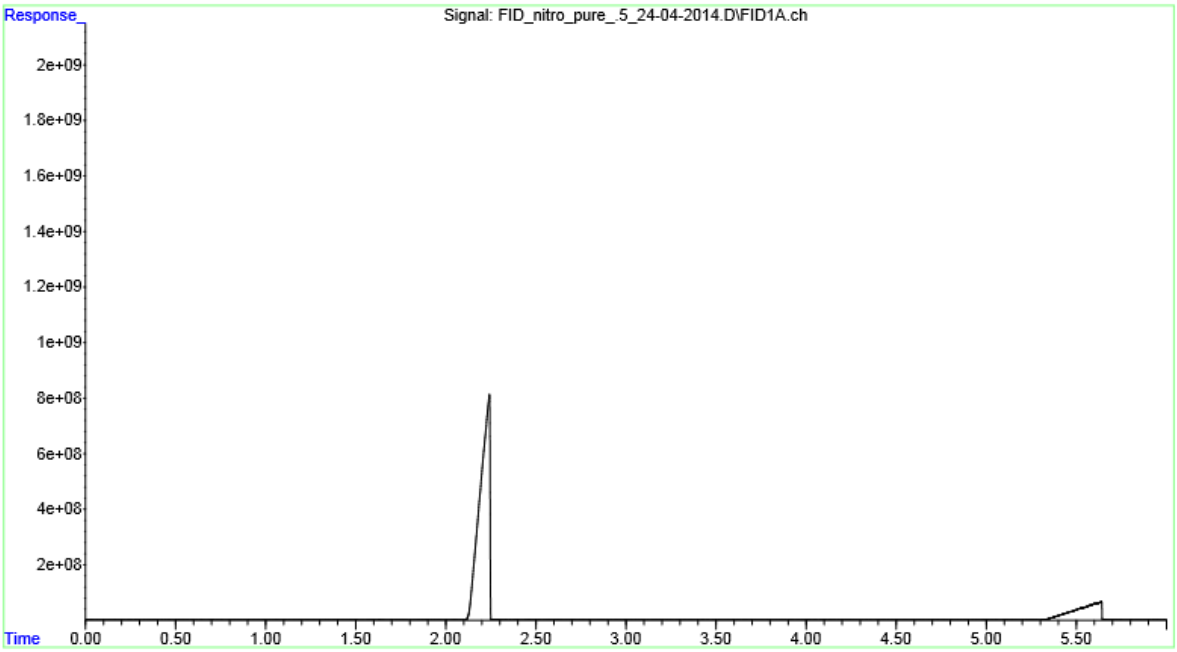


Fig 3.5 Response vs Retention time (Calibration Curve)

The graph of Response to retention time of a sample collected after 5 min of reaction time is as shown in the figure Fig 3.6:

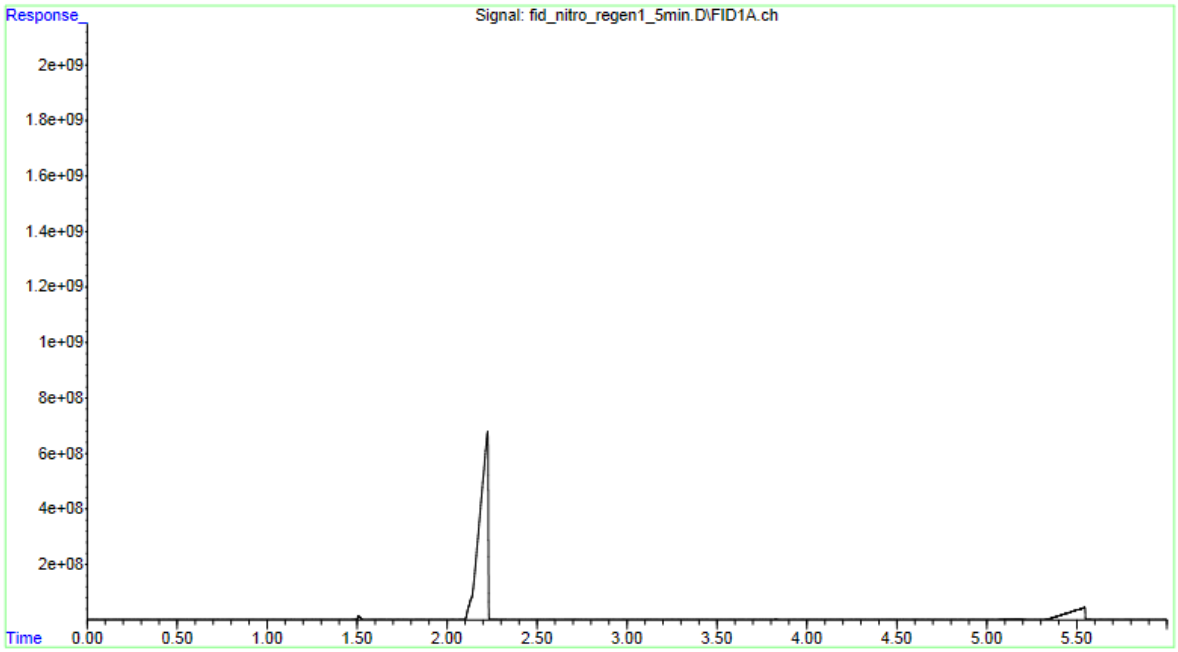


Fig 3.6 Response vs Retention Time (time = 5 mins)

The graph of Response to retention time of a sample collected after 480 min of reaction time is as shown in the figure Fig 3.7:

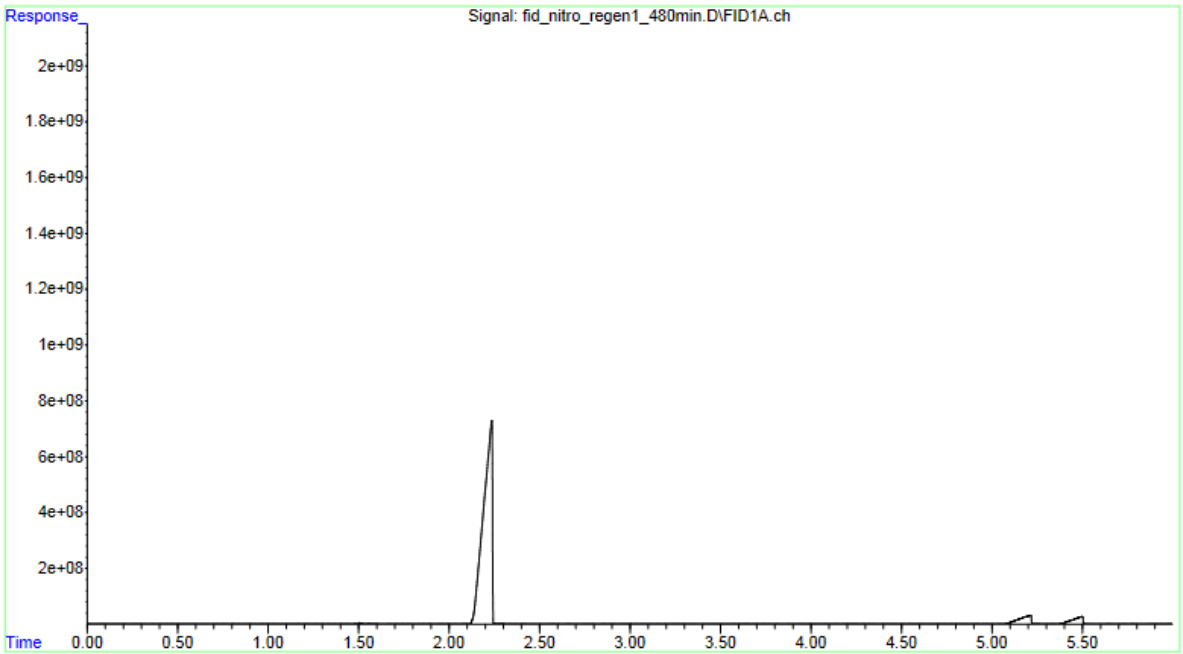


Fig 3.7 Response vs Retention Time (time = 480 mins)

The presence of a compound can be judged on the basis of retention time and its concentration is calculated by comparing the graph of the calibration sample and the sample under observation. The concentration can be calculated in two ways:

1. Peak% of max
2. % of total

CHAPTER 4

Reaction of Metachloronitrobenzene with H_2S absorbed in MEA in presence of Amberlite IR 400

4.1 ABSTRACT

This work focuses on the reaction of Metachloronitrobenzene with H_2S rich mono ethanol amine solution in presence of a tri phase catalyst (Amberlite IR 400) to produce metachloroaniline. The various parameters affecting the reaction are studied in detail and analysed. The parameters studied in the present work are Catalyst loading, Reactant (Metachloronitrobenzene) concentration, Temperature and Stirring speed.

4.2 INTRODUCTION

H_2S is generally separated from the sour gas to produce elemental sulphur. This process is known as Claus process. Although elemental sulphur is produced, the cost of this process is high because it involves stripping of the H_2S rich alkanolamine solution to give back the lean alkanolamine solution. However, if we use the absorbed H_2S solution to produce other chemicals which are beneficial to the chemical industry, then we need not spend a lot on production of elemental sulphur. Chloronitrobenzenes can be reacted with the solution to produce chloroanilines which are of great importance in manufacture of dyes and drugs.

Chloroanilines are of great importance when it comes to the manufacturing of dyestuffs, drugs and various types of pesticides. Chlorhexidine, which is a very important antimicrobial and bacteriocide is produced from chloroanilines. It is used in the manufacture of various types of pesticides like pyraclostrobin, anilofos, monolinuron and chlorphthali.Chloroanilines are also used in the manufacture of benzodiazepine drugs.

The chloronitrobenzenes and MEA are having varied specific gravities, thereby forming two different phases. If the reactants form two different phases, then the reaction becomes difficult for which we have to use a suitable catalyst. Literature review helps us to find out that a lot of liquid catalyst have been used for the reaction of benzyl chloride and H_2S rich MEA solution like Tetra Butyl Ammonium Bromide and Poly ethaline glycol, etc. The liquid catalysts cannot be separated easily from the solution after adding and hence purity of the product is not so good. This also creates a problem as quaternary ammonium compounds are harmful in liquid effluents. Liquid catalyst is lost after its use so cost of catalyst increases the cost of production. So considering the cost and purity of product solid catalyst has to be used. Amberlite is used as it is not much costly and is easily available.

4.3. RESULTS

4.3.1 Effect of Catalyst loading

The effect of concentration of catalyst (Amberlite IR 400) was studied in the present work. The catalyst plays a vital role in the conversion of MCNB to MCA. The effect of Amberlite IR 400 on the MCNB conversion was studied in the concentration range of 0.146-0.585M of organic phase, as shown in the figure Fig 4.1. From the graph plotted, it was found that the rate of conversion of MCNB to MCA increases with increase in concentration of catalyst, other parameters remaining constant. It was observed that when the catalyst to reactant ratio was 1 w/w then a conversion of 65 % is obtained which otherwise decreases to 52%, 38%, 33% with decrease in catalyst reactant ratio. The conversion % obtained with no catalyst is about 30 % which is very low as compared to the conversion obtained with 10gm catalyst. Hence, for all other reactions with different parameters under observation, 10gm catalyst is taken in the reactor. This observation can be a result of the decrease in mass transfer of the active species into organic phase which decreases with decrease in catalyst concentration.

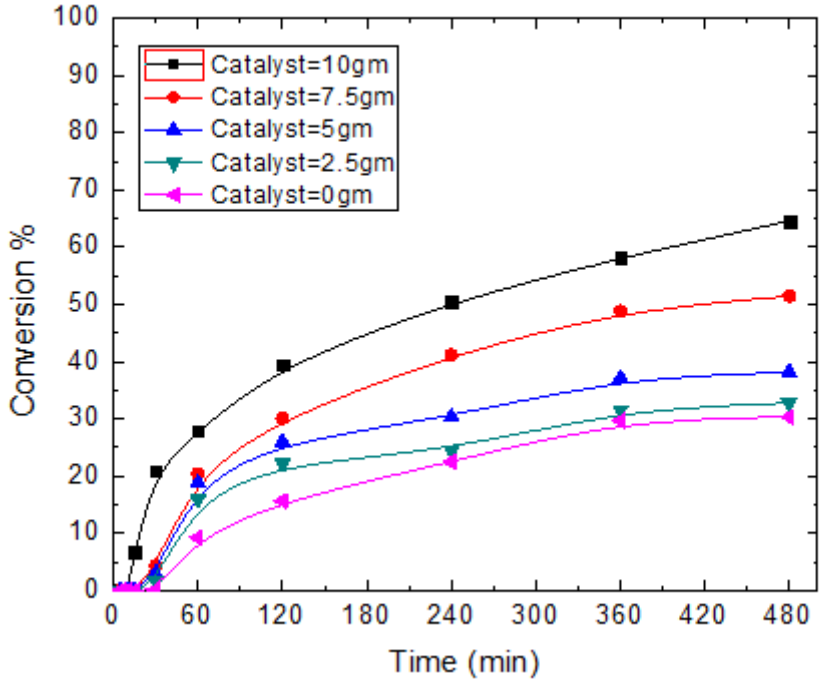


Fig 4.1: Effect of catalyst concentration on the conversion of MCNB

OPERATING CONDITIONS:

Vol. of organic phase = 50 ml, Vol. of aqueous phase = 50ml, concentration of reactant = 1.27M, Temperature = 50 ^{0}C, Stirring Speed = 1500 RPM, Sulphide Concentration = 2.53 moles/litre, MEA concentration = 5.787 moles/litre.

The order of the reaction with respect to the catalyst (Amberlite) concentration was also found out. The initial reaction rates were calculated for different concentrations of

catalyst. The natural logarithms of initial reaction rates were plotted against natural logarithms of initial Amberlite concentrations as shown in the figure Fig 4.1.1. Curve fitting method was applied to obtain a linear fit for all the points in the graph. The slope of the line is found out to be 0.9964, which is almost unity.

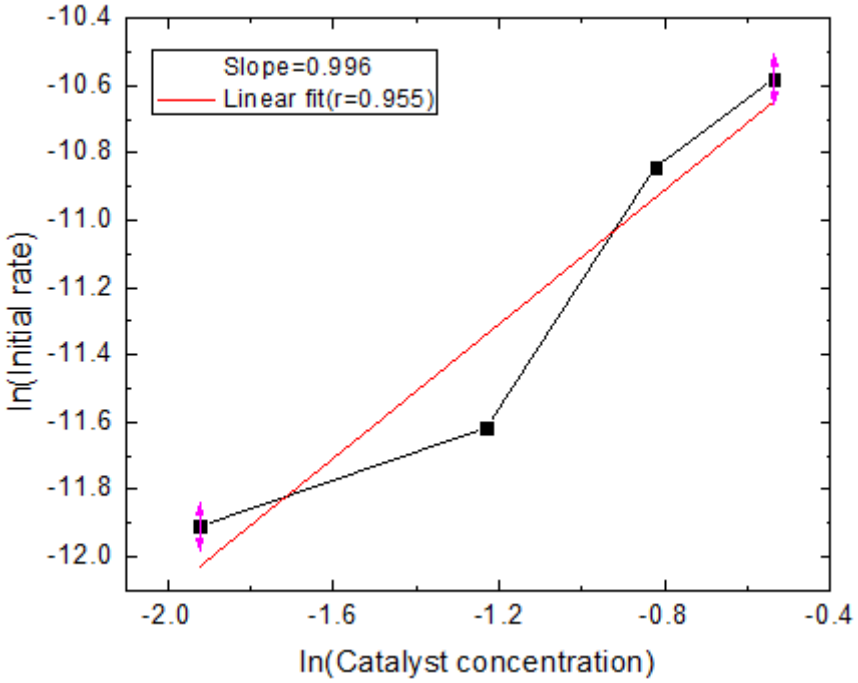


Fig. 4.1.1 ln(initial rate) vs ln(Catalyst concentration)

4.3.2 Effect of MCNB concentration

The concentration of reactant affects the rate and conversion of the reaction. The effect of MCNB concentration on the conversion of MCNB to MCA was studied at four different concentrations in the range of 0.31-1.27 M in the organic phase as shown in the figure Fig 4.2 . From the graph, it was observed that the conversion of MCNB decreases with increase in its concentration. The reason for this observation can be attributed to the sulphide content which is constant for all the cases, whereas the concentration of reactant varies. The increase in the concentration of the reactant with sulphide content remaining same leads to decrease in conversion of the reactant.

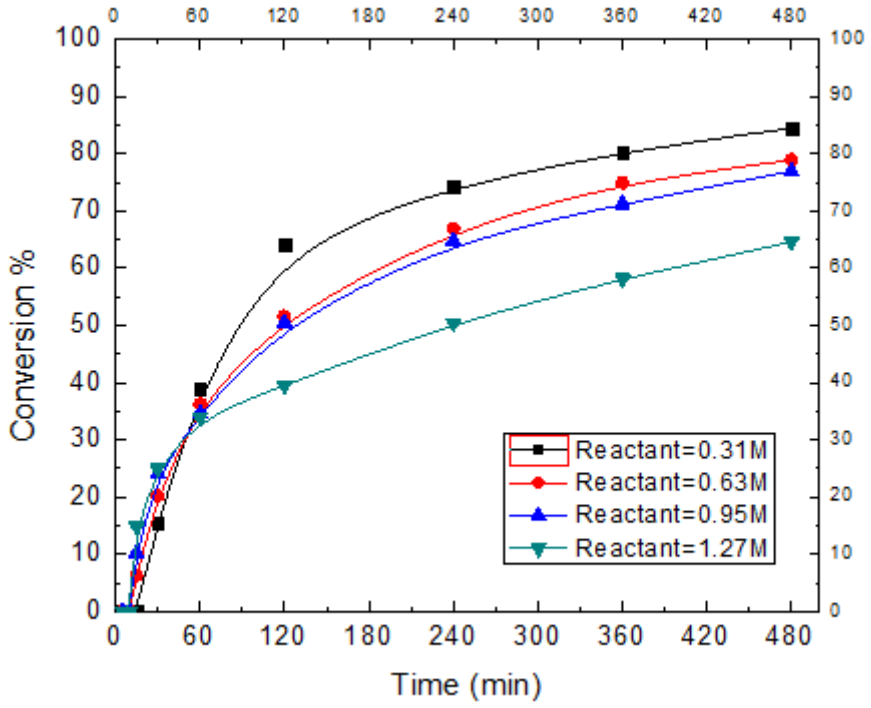


Fig 4.2: Effect of reactant on the conversion of MCNB

OPERATING CONDITIONS:

Vol. of organic phase = 50 ml, Vol. of aqueous phase = 50ml, Temperature = 50^0C, concentration of catalyst = 0.585 M, Stirring Speed = 1500 RPM, Sulphide Concentration = 2.53 moles/litre, MEA concentration = 5.787 moles/litre.

The order of the reaction with respect to the reactant (MCNB) concentration was also found out. The initial reaction rates are calculated at different reactant concentrations. The natural logarithms of initial reaction rates were plotted against the natural logarithm of the reactant concentration as shown in the figure Fig 4.2.1 . A linear fit is obtained for all the points in the graph. The slope of the line was found out to be 0.95, which is almost one.

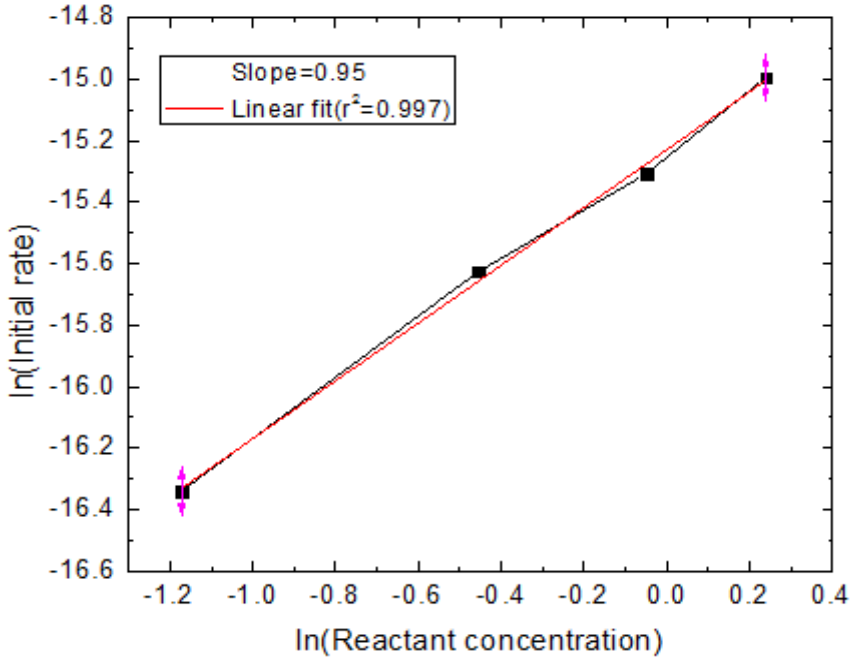


Fig. 4.2.1 ln(initial rate) vs ln(Reactant concentration)

4.3.3 Effect of temperature

The rate and conversion of a reaction is greatly influenced by temperature. The effect of temperature on the conversion of the reactant was studied in the range of 303-333 K with other parameters remaining the same. The graph between conversion and time was plotted as shown in the figure Fig 4.3 . From the graph, it was observed that the conversion of the reactant increases with increase in temperature. At 333 K, the conversion % attains a value of 80% which is relatively much higher than at lower temperatures.

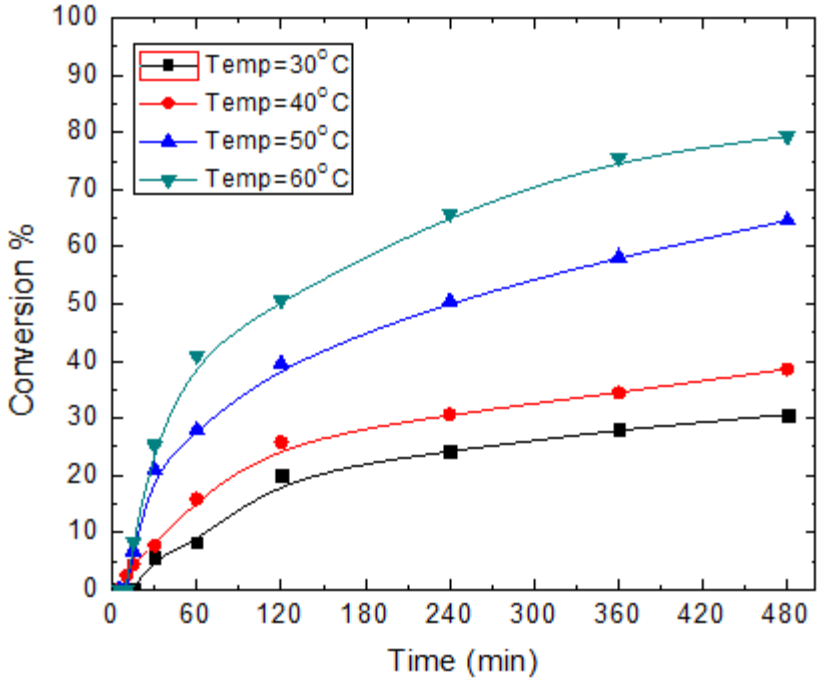


Fig 4.3: Effect of Temperature on the conversion of MCNB

OPERATING CONDITIONS:

Vol. of organic phase = 50 ml, Vol. of aqueous phase = 50ml, concentration of reactant = 1.27M, concentration of catalyst = 0.585 M, Stirring Speed = 1500 RPM, Sulphide Concentration = 2.53 moles/litre, MEA concentration = 5.787 moles/litre.

The reaction rate also increases with increase in temperature. Activation energy for the reactant in the reaction occurring can be calculated with the help of Arrhenius plot. Initial rates of reaction were found out for reactions occurring at different temperatures. The natural logarithms of the initial rates were plotted against 1/T as shown in the figure Fig.4.3.1c. A linear fit was obtained for all the points in the graph. The slope of this line is negative and equal to E/R, where E is the activation energy and R is the universal gas constant. With the help of the slope of the graph (which is -8968 in this case) activation energy was calculated to be 74.56 KJ/mol.

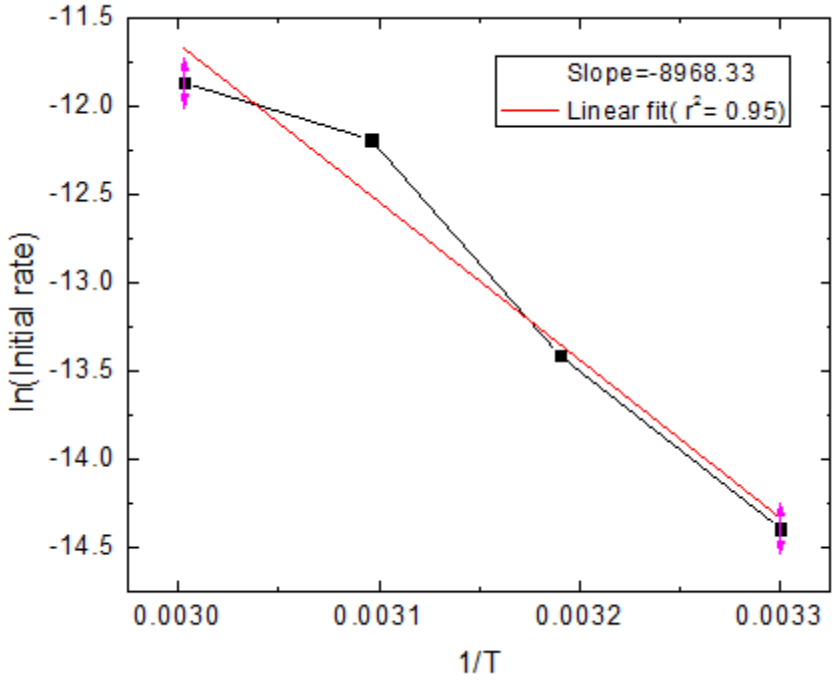


Fig. 4.3.1 activation energy for the reactant in the reaction

4.3.4 Effect of stirring speed

Mass transfer resistance builds up during the reaction if the contents of the reactor are not stirred. Hence it is very important to stir the contents of the reactor so as to eliminate mass transfer resistance which in turn is very important for kinetic study of the reaction. The effect of stirring speed was studied in the range of 1000-2000 RPM, with other parameters remaining the same. The graph of conversion versus time was plotted at different stirring speeds as shown in the Fig 4.4 . From the graph, it was observed that there is a little difference in the conversion with variation in stirring speed. Hence the mass transfer factor is negligible in this case. Stirring speed of 1500 RPM was maintained for all other reactions with different parameters under observation.

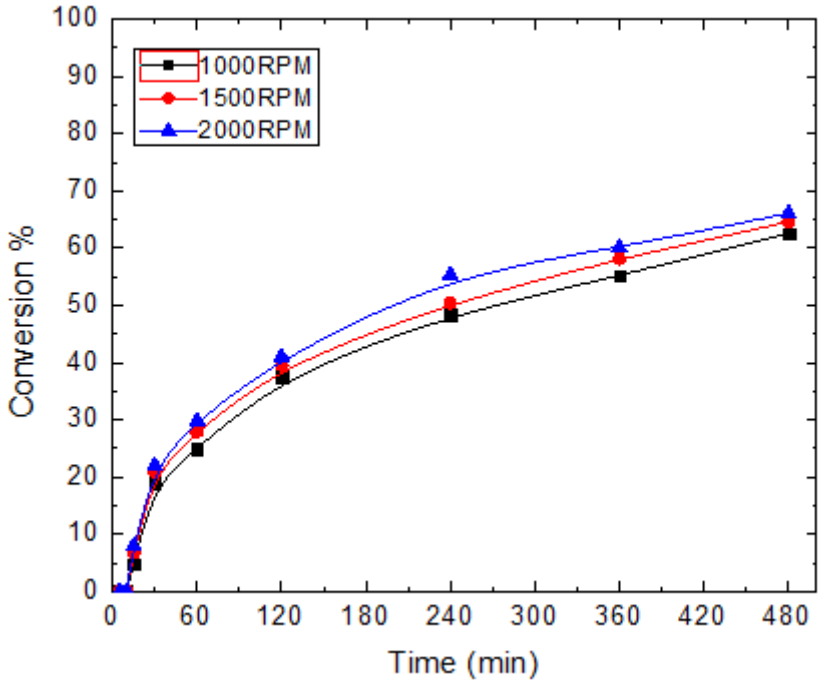
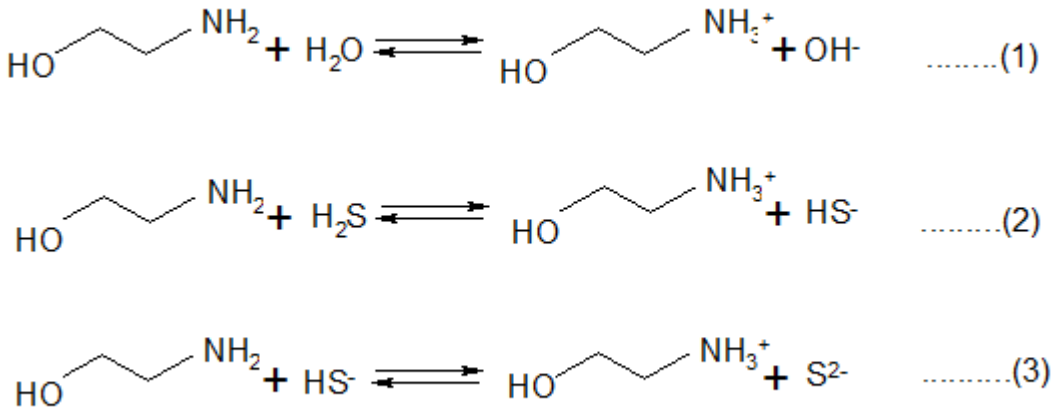


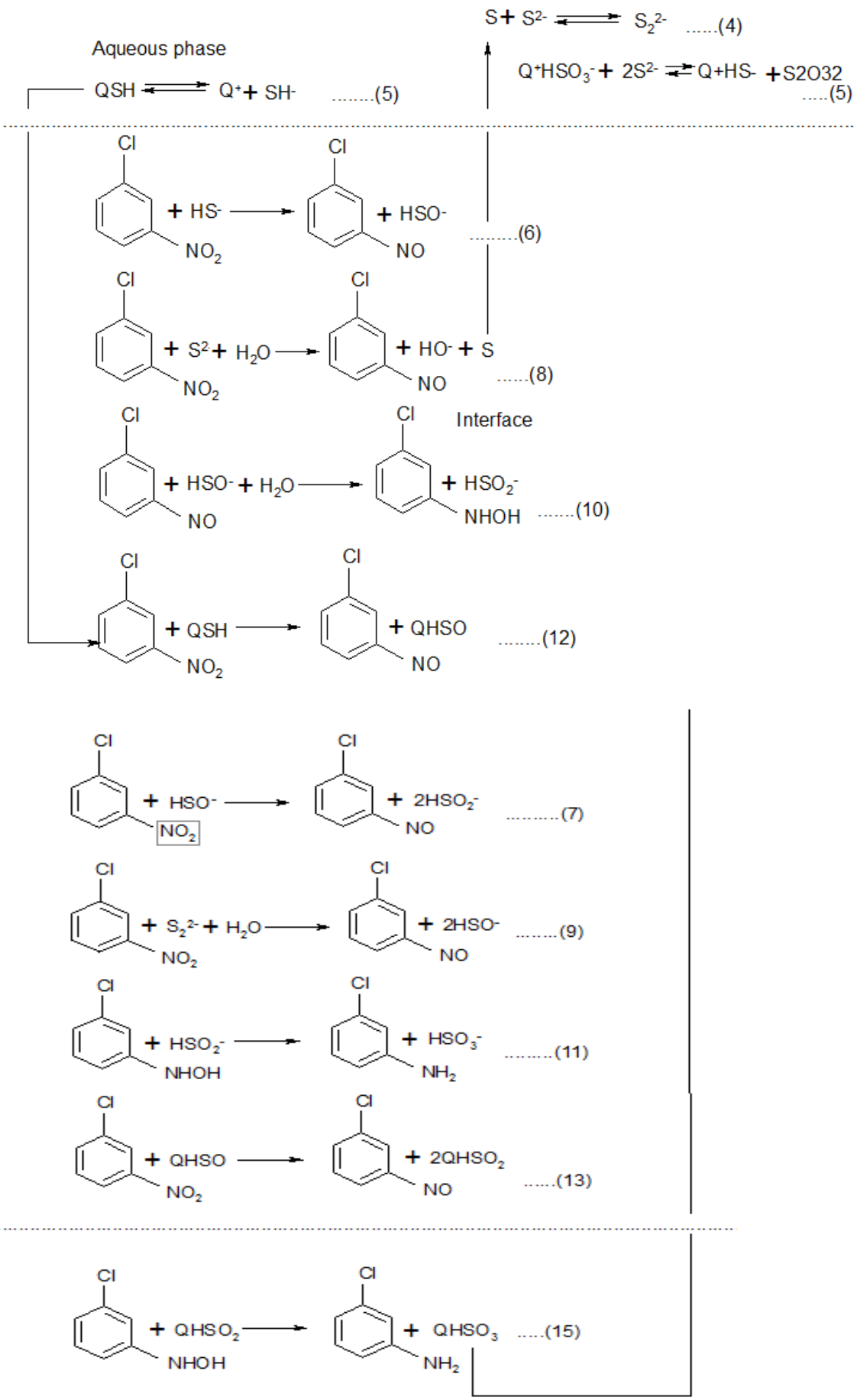
Fig 4.4: Effect of Stirring speed on the conversion of MCNB

OPERATING CONDITIONS:

Vol. of organic phase = 50 ml, Vol. of aqueous phase = 50ml, concentration of reactant = 1.27M, Temperature = 50 ^{0}C, concentration of catalyst = 0.585 M, Sulphide Concentration = 2.53 moles/litre, MEA concentration = 5.787 moles/litre.

4.4 REACTION MECHANISM




S + S2- ⇌ S2 2- .....(4)
Aqueous phase
QSH ⇌ Q+ + SH- .....(5)
Q+HSO3- + 2S2- ⇌ Q+HS- + S2O32 .....(5)
Cl
+ HS-
NO2
+ HSO-
NO
.....(6)
+ S2 + H2O
+ HO- + S
.....(8)
Interface
+ HSO- + H2O
+ HSO2-
NHOH
.....(10)
+ QSH
+ QHSO
.....(12)
+ HSO-
+ 2HSO2-
.....(7)
+ S2 2- + H2O
+ 2HSO-
.....(9)
+ HSO2-
+ HSO3-
NH2
.....(11)
+ QHSO
+ 2QHSO2
.....(13)
+ QHSO2
+ QHSO3
.....(15)

CONCLUSION

The reduction of metachloronitrobenzene by aqueous monoethanolamine solution to the corresponding chloroanilines was studied under Liquid-liquid-solid mode in presence of amberlite phase transfer catalyst. The chloroanilines are the only product found in the reaction.

The effect of various parameters on the rate of reactions and conversion of MCNB to MCA was while changing reactant concentration was S-shaped. This shows that the overall conversion decreases with increase in the reactant concentration whereas the initial rates o the reaction increases with increase in the reactant concentration. This inference is proved to be true from the plot of natural logarithm of initial reaction rate verses natural logarithm of reactant concentration.

The stirring speed does not much affect the conversion of reactants. The conversion was observed to be in the range of 62-67 % in the range of 1000-2000 RPM stirring speed. Hence the mass transfer factor is negligible here. The activation energy for metachloronitrobenzene was found to be 74.56 KJ/mol.Stirring speed of 1500 RPM was maintained for all other reactions with different parameters under observations.

Removal of H_2S from gases is required for reasons of health, safety, and corrosion during transmission and distribution and to prevent pollution with sulphur dioxide upon combustion of the gases. Chloroanilines are important building blocks used in the chemical industry for the production of pesticides, drugs, and dyestuffs. Therefore, the reduction of metachloronitrobenzene using Hydrogen sulphide and phase transfer catalyst will help us a get a very useful product.

FUTURE SCOPE OF THE PROJECT

This chapter throws light on the future scope of the project and how this project will help in the development of an industrial model for the use of hydrogen sulphide to produce fine chemicals with wide commercial applications.

The reduction reaction of metachloronitrobenzene was carried out with H_2S rich aqueous alkanolamine solution in presence of a liquid-liquid-solid tri phase transfer catalyst, Amberlite. The present work was regarding the determination of the effect of process parameters like stirring speed, catalyst concentration, concentration of the reactant and temperature.

The effect of other parameters could have been found out which are also necessary for determining the reaction mechanism and the dependence of reaction rate and conversion % on those parameters. Few of the other parameters which can be found out are

1. Effect of sulphide concentration
2. Effect of pH : pH regulates concentration of sulphide ion and hydrosulphide ion. The concentration of sulphide and hydrosulphide ion helps in determining the selectivity of the product.

The use of another solvent could have been considered. In this work, toluene has been used as the solvent. The choice of solvent plays a major role in the rate of the reaction as it influences the transport properties of the phase transfer catalyst and the active reactant species. Chlorobenzene and n-heptane can also be used as the solvents in future reactions.

Monoethanolamine solution was used in the present work to absorb hydrogen sulphide. Other aqueous solutions of methyl-diethanolamine and diethanolamine can also be used to absorb hydrogen sulphide to carry out the reaction.

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